

Synthesis of SiO_x Nanowires at Low Temperatures Using Zn Catalyst

Cham-Sol Choi and Jong-Hwan Yoon

Department of Physics, Kangwon National University,
Chuncheon, Gangwon-do 200-701, Republic of Korea, jhyoon@kangwon.ac.

ABSTRACT

Amorphous silica nanowires (NWs) were synthesized by simply annealing Zn film at 380°C for 10 min 10 silicon and oxygen chemical vapors produced by plasma-enhanced chemical vapor deposition technique using a mixture of SiH₄ and N₂O gas with fixed flow rates of 200 sccm and 60 sccm, respectively. The resulting NWs were shown to have a silicon-rich oxide (SiO_{1.34}) phase with a mean diameter of about 250 nm. It was also found that the NWs emitted light with its peak centered at 550 nm, consistent with that observed in silicon-rich oxide materials. It is proposed that the NWs are grown via ZnO-mediated vapor-solid process.

Keywords: silica nanowires, plasma-enhanced chemical vapor deposition, silicon-rich oxide

1 INTRODUCTION

Micro- and nanowires reveal various interesting physical and structural properties, and thus their properties have attracted considerable attention for potential application in nano-scale electric and optoelectronic devices. In particular, their large surface-to-volume ratio is of fundamental importance for improving the ability of devices such as the conversion efficiency of solar cells [1, 2]. Amorphous silica nanowires (NWs) also possess various excellent properties such as blue light emission, biocompatibility, and physical/chemical stability. These properties led the NWs to various applications, such as blue light emitter [3], optical waveguides [4], and biological and environmental sensing elements [5]. As a result, a wide range of techniques has been developed to synthesize silica NWs [3, 6-9]. A catalytic-assisted technique via vapor-liquid-solid (VLS) mechanism [10] is most generally employed for the growth of NWs. In this case, however, depending on the catalyst, high temperature thermal treatments are required. The metal-catalyzed technique using Si wafer coated with metal film, where NW growth is achieved by depositing a thin metal film on Si wafer and annealing the resulting structure at high temperatures in a high purity Ar or N₂ purging ambient, is suitable for easily

producing a large-scale of NWs, but thermal annealing should be performed at temperatures higher than the eutectic temperature of metal-Si alloy. For example, In the case of Ni-catalyzed growth, thermal annealing at over 1000°C at least should be required [11]. This high temperature annealing stage is a limiting factor in the application of NWs.

In this work, we report the synthesis of silica NWs by simply annealing Zn film at 350°C in silicon and oxygen chemical vapors. The vapors were simply produced by a conventional plasma enhanced-chemical vapor deposition (PECVD) method using a mixture of SiH₄ and N₂O gas. The resulting NWs were shown to have a large diameter of about 250nm. Contrary to the results (such as tips containing metal) that were usually observed in the vapor-liquid-solid process, it was found that there were no traces of Zn in the tips of the NWs. Instead, Zn was found in the body of NWs. A ZnO-mediated vapor-solid (VS) process is proposed for the present silica NWs.

2 EXPERIMENTAL

Silica NWs were grown in a conventional plasma-enhanced chemical vapor deposition (PECVD) system with capacitively coupled two electrodes. The top electrode of the reactor is coupled to a radio frequency (RF) power generator (13.56 MHz). The (100)-oriented *p*-type Si wafers (0.4 Ω-cm ~ 0.9 Ω-cm) coated with Zn(300 nm thick) are placed on the bottom electrode, which is grounded and placed at a 20 mm distance from the top electrode. The Zn film was prepared by thermal evaporation using high purity Zn metal (99.99%). A mixture of 5% SiH₄ in N₂ and N₂O gas was used as sources of silicon and oxygen for silica NW growth, respectively. The mixture of SiH₄ and N₂O gas was achieved by using fixed flow rates of 200 sccm and 60 sccm, respectively. The plasma power, the reactor pressure, and the substrate temperature during NWs growth were 290 mW/cm², 1.5 Torr, and 380°C, respectively.

The morphologies of the silica NWs were analyzed by using a field-emission scanning electron microscope (SEM) and a field-emission transmission electron microscope

(TEM) with energy-dispersive x-ray spectrometer (EDX). EDX and x-ray diffraction (XRD) spectroscopy were performed for phase analysis. The light emission properties of the silica NWs were analyzed using photoluminescence (PL) measurements at room temperature. The PL spectra were measured using the 325 nm line of a He-Cd laser as the excitation source. The He-Cd laser was focused on a sample area of about 1 mm² with a power density of 1.0 W/cm². Emitted light was collected with a lens and was analyzed using a grating monochromator and a photomultiplier tube (PMT: R928, Hamamatsu).

3 RESULTS AND DISCUSSION

Figs. 1(a) and 1(b) show SEM images of as-synthesized NWs at low- and high magnification, respectively. The images clearly show that the sample is found to be covered in a network of NWs having an average diameter of about 250 nm. However, as seen in Fig. 1(b), the NWs do not seem to have tips containing Zn, which induces the growth of NWs as the NWs are formed via VLS mechanism. This feature of not showing tips is very similar to that of the nanostructures grown by direct deposition of source vapors via vapor-solid process such as ZnO nanostructures [12, 13]. The results suggest that the growth of the NWs could be dominated by the VS process rather than the VLS mechanism.

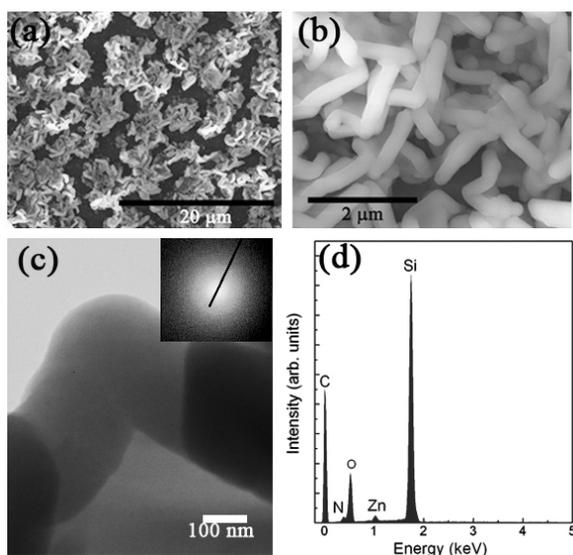


Figure 1. (a) Low-, (b) high-magnification SEM images of as-grown silica NWs, (c) TEM image and electron diffraction pattern (inset) taken on individual NWs, (d) EDX spectrum of as-grown NWs.

The detailed phase of the NWs was analyzed by TEM and EDX measurements, as shown in Figs. 1(c) and 1(d), respectively. Fig. 1(c) shows TEM and electron diffraction (ED) pattern (inset) taken on individual NWS. Fig. 1(d) shows the EDX spectrum taken from the individual NWs using EDX spectrometer attached to the TEM. It is clearly seen from Fig. 1(c) that the NW is homogeneous without any particles. Furthermore, the ED pattern reveals highly diffusive ring, demonstrating that the NWs are at a completely amorphous phase, which is composed of Si and O as shown Fig. 1(d). The EDX analysis showed that the composition ratio of Si and O is 1:1.34. On the other hand, the EDX data evidently shows that the NW contains N and Zn besides Si and O. The N may come from the source gases of SiH₄ and N₂O, while Zn is due to the Zn film. However, it was found that the Zn peak disappears after etching the NWs with HCl solution (not shown). Here, it should be noted that the as-grown NWs contain Zn atoms. The Zn-related peak can be due to the Zn film, but there is no such possibility because the size of the NWs is much larger than that of electron beam (~5 nm). As a result, the Zn-related EDX peak is due to the Zn atoms located on the surface of the NWs.

Figure 2 shows the PL spectra of as-synthesized NWs (blue color) taken at room temperature together that of NWs (blue color) etched in HCl solution for 6 min for comparison. The as-synthesized sample reveals two apparent PL peaks located near 550 nm and 380 nm. For the etched sample, however, it is found that the 550 nm PL peak remains unchanged but the 380 nm PL peak is negligible.

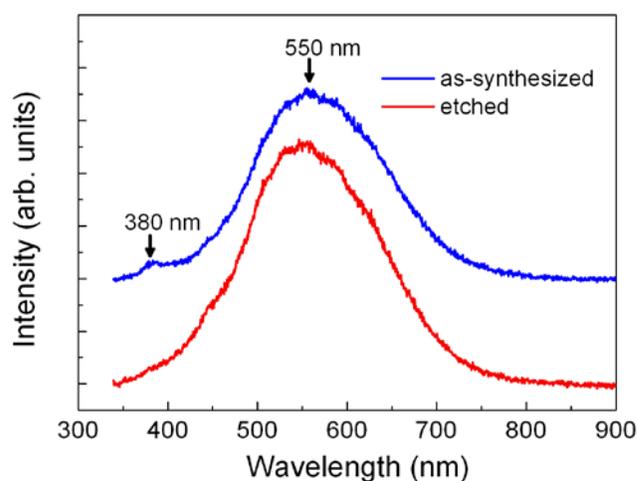


Figure 2. PL spectra of silica NWs before (as-synthesized) and after (etched) etching with HCl solution. Note that there is evident difference in the 380 nm peak between two samples.

Amorphous silica is generally shown to have several luminescence bands with peak energies ranging from 1.9 to 4.3 eV depending on the type of defects [14]. In particular, the 550 nm band is indicative of the no-bridging oxygen hole centers in silicon-rich oxide materials [15]. The appearance of a broad PL band with a 550 nm peak, which falls well within the range of PL data reported previously, supports the premise that the NWs have amorphous silicon-rich oxide phase, consistent with the data shown in Fig. 1(d). On the other hand, it is well known that the PL peak around 380nm is due to ZnO phase, which is apparently observed in the as-synthesized sample as shown in Figs. 1 and 2.

The presence of ZnO in the as-synthesized NWs can be further confirmed by x-ray diffraction spectroscopy (XRD) analysis. Fig. 3 shows representative XRD spectra of the silica NWs before and after etching with HCl solution as described previously. The XRD data of as-synthesized sample clearly shows several small peaks at a close range, and a large sharp peak and a broad peak, which arise from the Si substrate and the x-ray beam scattered from Si substrate, respectively. The small peaks were indexed using the index codes of ZnO crystal (ICDD No. 01-075-0576). The indexes shown in Fig. 3 represent those corresponding to the ICDD peaks. As seen in Fig 3, the small XRD peaks are in good agreement with those of ZnO crystal, demonstrating the presence of ZnO in the as-synthesized NWs as shown in Fig. 2.

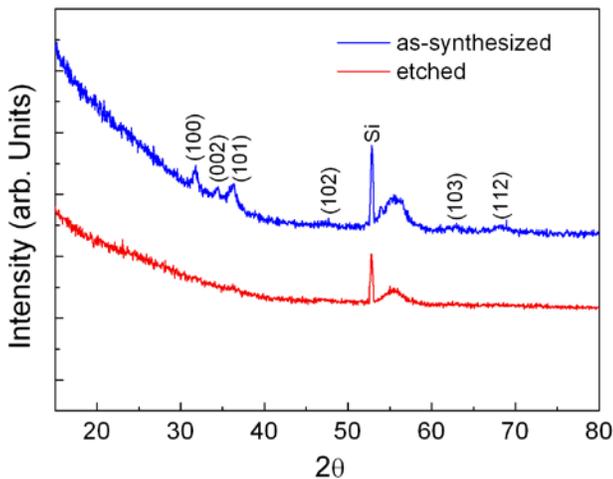


Figure 3. XRD spectra of silica NWs before (as-synthesized) and after (etched) etching with HCl solution. Note that the ZnO-related peaks completely disappear in the etched sample. The remaining sharp and broad peaks are due to the Si substrate and the x-ray beam scattered from Si.

The growth of silica NWs is generally believed to proceed via a vapor-liquid-solid (VLS) or vapor-solid (VS) growth mechanism depending on the catalyst employed. A typical evidence of metal-catalyzed VLS mechanism is that a metal particle is located at the tip of the wire and acts as the catalytic active site. This process also requires the formation of metal droplets. In this work, however, no Zn droplets are observed. Our results also show that there are no tips containing Zn in the NWs. These facts demonstrate that the NWs growth is unlikely to be governed by the VLS process. On the other hand, it has been found that silica NWs are never formed by the presented method without Zn film. This fact demonstrates that Zn plays an important role in the formation of silica NWs when the present method is employed. Furthermore, the presented various studies on the NWs clearly show the presence of Zn atoms on the surface of the NWs. This suggests a possibility that the growth of silica NWs could be closely related to Zn atoms. From the results, a possible mechanism based on VS process, namely, ZnO-mediated VS mechanism, is suggested for the growth of the silica NWs. First, Zn reacts with oxygen chemical vapors produced by PECVD via the reaction $Zn(s) + O(g) \rightarrow ZnO(s)$, forming ZnO particles acting as the nuclei sites of silica NWs growth, and secondly the ZnO particles react with Si chemical vapors, creating SiO_2 particles acting as the precursors for silica NWs growth, via the reaction $2ZnO(s) + Si(g) \rightarrow SiO_2(s) + ZnO(s)/Zn(g)$, where (s) and (g) denote the solid and gas phases, respectively. The Zn/ZnO located on the surface of the NWs, as shown in the previous data, is probably ZnO(s) produced by the latter reaction. According to this suggestion, the latter reaction can't be preceded without Si vapors. In particular, these reactions can be occurred at low temperatures. As a consequence, it is possible to fabricate silica NWs at low temperature using the present method.

4 SUMMARY

In conclusion, silica nanowires are simply synthesized by thermally annealing Zn film at a low temperature of $\sim 350^\circ C$ in oxygen and silicon vapors produced by PECVD using a mixture of SiH_4 and N_2O gas. The resultant NWs were shown to be composed of amorphous silica with a composition of $SiO_{1.34}$. The NWs were also shown to have a large diameter of about 250 nm, and emit broad light with a peak at around 550 nm. A possible mechanism based on the vapor-solid process, namely, ZnO-mediated vapor-solid process, was proposed for the silica nanowires growth.

Acknowledgement This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (Grant Number: 2010-0021320).

REFERENCES

- [1] M. Law, L. E. Greene, J. C. Johnson, R. Saykally, P. Yang, *Nature Mater.* 4, 455, 2005.
- [2] M. C. Putnam, S. W. Boettcher, M. D. Kelzenberg, D. B. Turner-Evans, J. M. Spurgeon, E. L. Warren, R. M. Briggs, N. S. Lewis, H. A. Atwater, *Energy Environ. Sci.* 3, 1037, 2010.
- [3] D. P. Yu, Q. L. Hang, Y. Ding, H. Z. Zhang, Z. G. Bai, J. J. Wang, Y. H. Zou, W. Qian, G. C. Xiong, S. Q. Feng, *Appl. Phys. Lett.* 73, 3076, 1998.
- [4] D. P. Yu, Q. L. Hang, Y. Ding, H. Z. Zhang, Z. G. Bai, J. J. Wang, Y. H. Zou, W. Qian, G. C. Xiong, S. Q. Feng, *Nature* 426, 813, 2003.
- [5] F. Patolsky, G. Zheng, C. M. Lieber, *Nanomedicine* 1, 51, 2006.
- [6] K-H Lee, H. Soo. Yang, K. H. Baik, J. Bang, R. R. Vanfleet, W. Sigmund, *Chem. Phys. Lett.* 383, 380, 2004.
- [7] Z. Pan, S. Dai, D. B. Beach, D. H. Lowndes, *Nano Lett.* 3, 1279, 2003.
- [8] Z. L. Wang, *Adv. Mater.* 15, 432, 2003.
- [9] T.-H. Kim, A. Shalav, R. G. Elliman, *J. Appl. Phys.* 108, 076102, 2010.
- [10] R. S. Wagner, W. C. Ellis, *Appl. Phys. Lett.* 4, 89, 1964.
- [11] A. A. Istratova, P. Zhang, R. J. McDonald, A. R. Smith, M. Seacrist, R. Wahlich, E. R. Weber, *J. Appl. Phys.* 97, 023505, 2005.
- [12] Z. W. Pan, Z. R. Dai, Z. L. Wang, *Science* 291, 1947, 2001.
- [13] Z. L. Wang, *J. Phys.: Condens. Mater.* 16, R829, 2004.
- [14] H. Nishikawa, T. Shiroyama, R. Nakamura, Y. Ohki, K. Nagasawa, Y. Hama, *Phy. Rev.* B45, 586, 1992.
- [15] L. Vaccaro, M. Cannas, V. Radzig and R. Boscaino, *Phys. Rev.* B78, 075421, 2008.